1944

The combustion of phosphorus

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Recommended Citation

Hoeman, Erwin Charles, "The combustion of phosphorus" (1944). *Professional Degree Theses*. 284.
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THE COMBUSTION OF PHOSPHORUS

BY

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A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

CHEMICAL ENGINEER

Rolla, Missouri

1944

Approved by W. T. Schrenk.

Chairman, Department of Chemistry and Chemical Engineering.

ACKNOWLEDGMENT

The author gratefully acknowledges the experience gained in the production and utilization of phosphorus, through his employment in the Department of Chemical Engineering of the United States Tennessee Valley Authority. Specifically, he acknowledges the supervision of work and inspiration gained through his association with Dr. Raymond L. Copson, Chief of the Research and Development Division; Dr. Grady Tarbutton, Assistant to the Chief; and Mr. John H. Walthall, Head of the Development Section.

Particular thanks for guidance in the selection of the general plan for this paper are due to Mr. J. F. Shultz, formerly Chemist with the United States Department of Agriculture, and now Chemist in the organization of the United States Tennessee Valley Authority.

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THE COMBUSTION OF PHOSPHORUS

Introduction

Phosphorus first joined the ranks of large-tonnage industrial raw materials about ten years ago, with the development of the electric furnace method for its production from rock phosphate. For many years before the present era of large-scale production, phosphorus had been little more than a laboratory curiosity. Thereafter, it found extensive application in pyrotechnics, match tips, rat poisons, and other uses not requiring more than a few hundreds of tons in a year. Phosphoric acids were generally produced by the reaction of sulfuric acid with rock phosphate. The development and growth of electrothermal processes for the reduction of rock phosphate completely changed the method of producing phosphoric acids. Phosphorus, produced in electric furnaces, is now an industrial commodity that may be burned to the oxide, then hydrated to phosphoric acids, and finally converted into a great number of phosphate compounds.

A brief catalogue of the significant events leading up to the present state of development of the electric-furnace process for the production of phosphorus is shown in the following table:

Table 1

Significant Events in the History of Phosphorus

Year	Event
1669	Brandt discovered phosphorus.
1775	Scheele produced phosphorus from bones.
1829	Wohler produced phosphorus experimentally by heating calcined bones with sand and carbon.
1867-79	Early English and French patents on the thermal reduction of phosphates appeared in the literature on the subject.
1890	Phosphate reduction was brought to a stage of practical development by Readman and others (German patents), and the first use was made of an electric furnace to smelt a mixture of phosphate, coke, and silica.
1920	The first electric furnace plant for the reduction of rock phosphate, in the United States, was installed at Anniston, Alabama, by Swann Chemical Company (acquired later by the Monsanto Chemical Company).
1934	Electric furnace processes for making phosphorus were first adapted to the manufacture of phosphate fertilizers, at Wilson Dam, Alabama, by the United States Tennessee Valley Authority.

The Monsanto Company, the Tennessee Valley Authority, and the Victor Chemical Company, all of which now have furnace plants near the Tennessee phosphate fields, were the pioneers in the production of phosphorus on a large scale. The Victor Company, notably, also has pioneered in the production of phosphorus by thermal reduction of rock phosphate in the blast furnace. The future of the blast-furnace method for the production of phosphorus, however, is at present uncertain. Apparently, it cannot compete with the electric-furnace method in areas located near low-cost electric energy.

Statistical data on the production of phosphorus are not obtainable from the records of the United States Census, chiefly because of the small number of primary producers. Based on news accounts (1) and personal sources of information, it appears that the production of phosphorus has increased about seven-fold in the decade from 1930 to 1940, or as shown in the following table:

Table 2

Installed Capacity for the Production of Phosphorus in the United States

(Tons per annum)

Year	Blast Furnace	Electric Furnace TVA	Electric Furnace Industry	Total
1930	8,000	-	2,000	10,000
1935	8,000	8,000	2,000	18,000
1936	11,000	8,000	26,000	45,000
1937	11,000	12,000	26,000	49,000
1938	-	12,000	37,000	60,000
1939	-	16,000	38,000	54,000
1940	-	16,000	49,000	65,000
1941	-	16,000	57,000	73,000

Military uses for phosphorus, now in a time of war, take practically the entire output of phosphorus. Additional production capacity has been installed since 1941, and increased production is being obtained from all installations. It is probable that present production exceeds 100,000 tons per annum.

The story of the development of processes for the electric-furnace production of phosphorus and its subsequent utilization is an extremely interesting account of chemical engineering achievement.

The contributions of the Tennessee Valley Authority to phosphorus and phosphate developments are particularly thoroughly covered in a series

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(1) Largely from the News Edition of Industrial and Engineering Chemistry.

of articles, describing the Wilson Dam Plant (2-9).

The plant constructed at Muscle Shoals, Alabama, for the United States Government at the close of World War I was converted into a plant to manufacture phosphorus and phosphate fertilizers as a part of the regional development program of the Tennessee Valley Authority. The original plant was designed to make ammonia by the calcium cyanamide process, and to utilize the ammonia to manufacture ammonium nitrate for munitions. Obviously, the plant in its original form was a wartime asset, and the problem of converting it for phosphorus production had to be met in a way not to prevent its possible future

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(2) Curtis, H. A. TVA makes H_3PO_4 electrically at Wilson Dam. Chem. Met. Eng. v 42, pp. 320-324 (1935).

(3) Curtis, H. A. Making concentrated superphosphate at TVA Fertilizer Works. Chem. Met. Eng. v 42, pp. 488-491 (1935).

(4) Curtis, H. A., and Miller, A. M. Operating observations at TVA Fertilizer Plant. Chem. Met. Eng. v 43, pp. 408-412 (1936).

(5) Miller, A. M., and Junkins, J. N. TVA estimates favorable costs for concentrated superphosphate. Chem. Met. Eng. v 43, I. pp. 583-587 and II. pp. 647-650 (1936).

(6) Curtis, H. A., Miller, A. M., and Newton, R. H. TVA reviews its experience in phosphate smelting. Chem. Met. Eng. v 45, pp. 116-120 (1938).

(7) Curtis, H. A., Miller, A. M., and Newton, R. H. Process developments at TVA phosphoric acid plant. Chem. Met. Eng. v 45, pp. 193-197 (1938).

(8) Newton, R. H. TVA's phosphate smelting results. Chem. Met. Eng. v. 45, pp. 374-379 (1938).

(9) Curtis, H. A., and Heaton, R. C. Design for a phosphate furnace. Chem. Met. Eng. v 45, pp. 536-540 (1938).

reconversion for munitions production. The management succeeded in solving this problem in conversion. In fact, as measured by the demands of the present war, it has added to the munitions production value of the plant by making it a source of munitions phosphorus as well as ammonium nitrate.

The purpose of this paper is to present a review and discussion of phosphorus as a raw material with particular reference to its combustion and conversion thereby into other useful materials. The greater part of the author's experience with phosphorus has been in the operation of large pilot plants in which phosphorus combustion was an important factor, including the research attendant upon the development of the several processes for burning phosphorus.

The Production of Phosphorus in Electric Furnaces

Phosphorus furnaces at the Wilson Dam plant were constructed in the building that originally accommodated the twelve calcium carbide furnaces. Five of the original carbide furnaces were replaced by phosphorus furnaces. It is apparent, therefore, that the arrangement of furnaces for phosphorus production was controlled by the facilities existent for carbide production.

Calcium carbide furnaces have open tops with the charge delivered to a floor level with the furnace top and loaded into the furnaces as required for their operation. Electrodes are suspended directly into the furnace, and have their lower, free-hanging ends submerged in the burden of lime and coke. Suction fans draw the gases from the open furnace tops. The calcium carbide is tapped through tap holes, placed near the furnace bottoms, directly into chill cars running on tracks on the floor of the furnace building.

The phosphorus furnaces, with closed tops, were constructed at calcium carbide furnace sites. The electrodes for these furnaces pass through the furnace roof, and ducts for drawing off the furnace gases are provided near one end and near the top of each of the five furnaces. Slag and ferrophosphorus metal, byproducts of phosphorus production, are drawn off through tap holes provided near the base of each furnace.

Phosphorus Furnace Design

All of the elements in the general design of phosphorus furnaces have been presented and illustrated in a publication by members of the staff of the Tennessee Valley Authority (10), and will not be repeated here.

The best size and shape for an electric furnace producing phosphorus are not definitely known. The clearance between electrode surfaces must be sufficient to prevent any considerable passage of current directly from electrode to electrode. The desired flow of current is from each of the three electrodes through the burden to the ground, thus concentrating heating and melting in the bottom of the furnace and providing for the maintenance of a pool of molten slag and ferrophosphorus metal to be drawn from the furnace by tapping. Electrodes in the Tennessee Valley Authority furnaces are spaced about 6 feet from center to center.

Cylindrical and rectangular shapes have been used in furnace design. At the Wilson Dam plant, one of the furnaces is cylindrical, and the other four furnaces are rectangular. The latter shape is favored for several reasons including the advantage of more working space and better arrangement of feed chutes at the furnace top.

Four of the five furnaces are of 6,000-kilowatt capacity and the other one of 12,000-kilowatt capacity. Six kilowatt hours of electric energy are required to produce one pound of phosphorus, as established by many checks of energy and material balances in the operations of the furnaces. Thus, each of the 6,000-kilowatt furnaces produces 12 tons, and the 12,000-kilowatt furnace produces 24 tons of phosphorus each day. Operated at full capacity for an 11-month year

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(10) See footnote 9.

(one month in each year is required to reline and recondition a phosphorus furnace), the Tennessee Valley Authority phosphorus plant produces approximately 16,000 tons of phosphorus. (One of the furnaces does not have a phosphorus condensing system, and the gases from the furnace are burned directly).

Phosphorus Furnace Operation

Rock phosphate is received at the plant by rail shipment from the fields and washing plants in Tennessee. The operation of the furnaces require that the phosphate be in lump form, therefore natural lumps are preferred. However, the exploitation of the Tennessee deposits has very nearly exhausted the supply of plate rock which is broken into lumps in the mining and handling operations. Practically all of the phosphate now used consists of washed sands which must be agglomerated into lumps for subsequent use in the furnaces.

Experiments have been made on the composite agglomeration of the constituents (rock phosphate, silica, and coke) into lumps for the furnace burdens, but the results were not satisfactory. These composite lumps did not handle well in the furnaces. In present operations, lump phosphate, silica pebbles, and screened coke are prepared separately and mixed in bins prior to charging to the furnaces.

The phosphate sands are agglomerated either by sintering on Dwight-Lloyd sintering machines or by nodulizing in rotary kilns. The Tennessee Valley Authority prefers agglomerates produced by nodulizing, principally because large rotary kilns, provided originally for calcining limestone to produce lime to be used for calcium carbide production, were available at the Wilson Dam plant. In addition, tests appeared to indicate that nodules are superior to sinter in phosphorus furnace burdens.

Carbon monoxide gas, produced as a byproduct of the phosphorus furnace operations, is used, with some powdered coal, as the fuel for nodulizing or agglomerating the phosphate sands. The practice of nodulizing phosphate sands in rotary kilns has been developed to a very high stage by the Tennessee Valley Authority. One of the major problems, that of the formation of accretions in the kilns, has been solved by providing mechanically operated cleaning bars that periodically or continuously remove deposits of fused and subsequently hardened phosphate from the kiln walls.

In producing the charge for the furnaces, the lump or agglomerated phosphate is mixed with a proper proportion of silica and coke to give a satisfactory slag composition. Experience has indicated that the proportions of the raw materials should be such that the slag has a SiO_2 to CaO weight ratio of 0.7 to 0.8, and that the coke should be sufficient to provide approximately 0.422 pound of carbon per pound of P_2O_5 and 0.222 pound of carbon per pound of Fe_2O_3. A small excess of coke, usually about 2 percent, is also allowed to provide for other reducible compounds in the burden and to minimize electrode consumption. Various details of the calculation of phosphorus furnace burdens are described in an article published in 1938 (11).

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(11) See footnote 8.

Several reactions occur in the electric furnace. Some of these are exothermic, as shown below, but the overall reaction is endothermic requiring electrical energy.

Table 3

Reactions in the Electric-Furnace Reduction of Rock Phosphate

1. $2\ Ca_3(PO_4)_2 + 10\ C = 6\ CaO + P_4 + 10\ CO$
2. $CaO + SiO_2 = CaSiO_3$
3. $3\ CaO + 2\ SiO_2 = Ca_3Si_2O_7$
4. $CaF_2 + SiO_2 = 2\ CaO + SiF_4$
5. $Fe_2O_3 + 3\ C = 2\ Fe + 3\ CO$
6. $Fe + P = FeP$
7. $2\ Fe + P = Fe_2P$

The overall furnace reaction is usually represented by the following equations:

$$2\ Ca_3(PO_4)_2 + 10\ C = 6\ CaO + P_4 + 10\ CO \text{ and}$$

$$X\ CaO + Y\ SiO_2 = (X-Y)\ Ca_3Si_2O_7 + (3Y-2X)\ CaSiO_3.$$

It is apparent from the second equation that variations in the ratio of silica to rock phosphate may be made to control the SiO_2 to CaO ratio of the calcium silicate slag.

The energy consumption in the electric furnace depends upon a number of variable factors which are described below from records of observations of the operation of the furnace plant:

(1) The P_2O_5 content of the burden is the principal factor influencing the consumption of energy. When the P_2O_5 content was increased from 25 percent to 28.5 percent, the energy consumption decreased

regularly from 5800 to 4200 kilowatt hours per ton of phosphorus pentoxide volatilized.

(2) Increase in energy load gave an increase in productive capacity for phosphorus. Although the energy requirement per ton of P_2O_5 reduced increases with increased load, as a result of increased heat losses, the increased capacity warrants the higher loads.

(3) Higher voltage permitted greater loads without increased current density. Higher voltage gave more efficient operation by spreading the heating in the furnace and by giving less electrode consumption per unit of P_2O_5 reduced. The limiting factor on voltage is the safety of the furnace personnel and the carrying over of dust from the furnace. Increasing the depth of the furnaces has permitted higher voltages without increasing the carrying over of dust from the furnace.

(4) Energy requirements are decreased by decrease in current density. The maximum allowable appears to be 32 amperes per square inch of electrode surface. Factors permitting this high value with efficient energy utilization are careful attention to making good electrode joints and maintenance of proper furnace pressure control.

Typical operating conditions and a heat balance for an electric furnace are shown in Table 4:

Table 4

Electric Furnace Operating Conditions and Heat Balance

Operating Conditions:

Energy load, kilowatts	6550
Arc voltage	125
P_2O_5 in rock phosphate and silica, percent	26.4
Furnace charge, tons of P_2O_5 per hour	1.41
Excess coke in charge, percent	2.1
Energy consumption, kilowatt-hours per ton of P_2O_5 charged	4635
Slag, SiO_2/CaO ratio	0.73
P_2O_5 in slag, percent	1.00

Heat Balance: (Basis: 1 ton of P_2O_5 in charge)

Heat Input	Btu. x 1,000,000	Percent of input
Electric energy	15.8	100.0
Heat Output		
Net chemical reactions	7.6	48.0
Heat in products:		
2.72 tons of slag at 2727° F.	4.6	29.0
0.218 tons of ferrophosphorus at 2727° F.	0.2	1.3
0.361 tons of P_4 at 706° F.	0.6	3.8
Cooling water:		
Electrodes, 4,440 lb. at 51° F.	0.2	1.3
Furnace shell, 18,300 lb. at 40° F.	0.7	4.5
Radiation and convection	0.1	0.7
Unaccounted for losses	1.8	11.4

Additional average operating data for an electric furnace, taken for a three months' period of operation for the same furnace as in Table 4, are shown in Table 5:

Table 5

Electric Furnace Operating Data

Energy load, kilowatts	6550
Kilovolt-ampere load (kilowatts/power factor)	7120
Transformer voltage	215
Arc voltage	125
Electrode current, amperes	19,300
Current density, amperes per square inch	27.2
Energy consumption, kilowatt hours	13,800,000
P_2O_5 charged: for entire period, tons	3000
per day, tons	34.6
P_2O_5 in slag, tons	80
P_2O_5 in ferrophosphorus, tons	120
P_2O_5 volatilized: for entire period, tons	2820
per day, tons	32.3
P_2O_5 in rock phosphate and silica, percent	27.5
Energy consumed: kilowatt hours per ton of P_2O_5 charged	4550
kilowatt hours per ton of P_2O_5 volatilized	4870
Electrode consumption, pounds per ton of P_2O_5 charged	16.0
Excess coke in charge, percent	3.9
Total days of operating time	87.5
Operating time, percent of total time	97.0

The average charge to the furnace over the test period shown in Table 5 was 33 percent rock phosphate, containing 31.6 percent P_2O_5, and 67 percent nodulized rock phosphate sands, containing 33.5 percent P_2O_5.

The slag and ferrophosphorus metal were tapped from the furnace at two-hour intervals, into a carbon-lined crucible wherein the metal settled by gravity. The slag overflowed from the lip of the crucible into a slag-handling duct wherein it was granulated and conveyed into a collecting basin by streams of high-pressure steam and water. The ferrophosphorus metal was poured and cast in pig molds, and was refined to remove silica by remelting with rock phosphate and lime in either a Detroit rocking electric furnace or a vertical-electrode furnace of conventional type.

Phosphorus Condensation and Handling

Phosphorus, as produced in the electric furnace, is at a temperature above its dewpoint in admixture with nearly pure carbon monoxide gas. This vapor and gas mixture can be burned directly in order to oxidize the phosphorus to phosphorus pentoxide to be converted into phosphoric acid, or, alternatively, the phosphorus can be condensed from the mixture and the carbon monoxide conserved for use as a fuel gas.

The characteristics and advantages and disadvantages of the two types of phosphorus-handling systems are described in a publication by Curtis, Miller, and Newton (12) of the staff of the Tennessee Valley Authority. A single furnace with an adjacent combustion chamber for burning the furnace gases directly was installed and is in operation up to the present time. Tests have shown, however, that no real economies in operation are realized, and phosphorus from all of the other furnaces is condensed from the gas stream and collected in solid form. Early in the development of phosphorus production at Wilson Dam, it was considered that the phosphorus might some day play an important part in military use, and, therefore would need be collected in solid form for transportation and use in theaters of war.

The collection and purification of phosphorus has entailed considerable experimentation to evolve suitable handling systems. Wet

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(12) See footnote 6.

condensation, that is, by water from sprays, originally appeared to be the most desirable method.

In wet condensation of phosphorus, the furnace gases are cooled, and phosphorus is condensed by water from sprays in a vertical, cylindrical condenser. The condensed water and phosphorus sludge is pumped to a Dorr thickener from which the phosphorus underflow is pumped to storage tanks and the water overflow back to the condenser for use as spray liquor. The residual gas, mostly carbon monoxide, is collected by fans and blown elsewhere for use as fuel gas.

Various operating difficulties developed in the application of this phosphorus condensing system. Potassium fluosilicate, gelatinous silica, phosphorus and dust accumulated in the recirculating condenser water and plugged the water pipe lines. This difficulty was corrected to a great extent, but not entirely, by making the thickener the coldest part of the system (by water cooling) and thus maintaining the other hotter parts of the system unsaturated with respect to the soluble impurities. Also, to aid in temperature control in the system and to clean deposits from the pipe lines, steam was injected into the liquor return line. The most important corrective treatment for the elimination of troubles due to impurities has been the use of agglomerated phosphate in the furnaces, as reduction and heating during agglomeration removes much of the fluorine from the phosphate, and decreases condenser troubles.

Phosphorus losses in wet condensation also were troublesome in the operation of this type of condenser. The first method tried was to install a tubular gas cooler in the pipe line carrying the exhaust gases from the condenser system. Plugging and corrosion of the equipment were severe. An Infilco entrainment separator was then installed. Difficulties due to plugging again were too severe to be tolerated. Finally, a Nash-Hytor pump and entrainment separator of the type often used for removing condensate from the return lines in steam heating systems was tried with excellent success. In the application of this system, the most of the phosphorus in the gases leaving the condensing system was collected in the pump.

With the installation of other electric furnaces, additional wet condensation systems were installed with slight changes in design but retaining the Dorr thickener for phosphorus sludge and the Nash-Hytor pump and entrainment separator systems.

As the work on phosphorus production progressed, it became increasingly apparent that better methods of collecting phosphorus and changes in operating technique to produce cleaner phosphorus were necessary. The product from wet condensation is a phosphorus sludge comprising a phosphorus-in-water emulsion stabilized by dust and fluosilicates. Various methods for filtering this sludge, to effect separation of water and impurities from the phosphorus, distillation, and chemical emulsion breaking were all tried with indifferent success. Use of the phosphorus sludge directly in phosphorus burning systems multiplied operating and corrosion difficulties.

Attention was drawn to the possibility of condensing the phosphorus from the furnace gases directly, out of the presence of water, in externally cooled tubular condensers. Small-scale work on the dry condensation of phosphorus demonstrated that the process was feasible, and the decision was made to use this system on a new furnace then being constructed. The application of a dry condenser system, however, required that the gas must be cleansed of impurities prior to phosphorus condensation.

Gas cleansing was accomplished by the use of electrostatic precipitators in the gas lines from the electric furnace. These were maintained at a temperature above the dewpoint of phosphorus in the gas by the use of external strip heaters. The system used was designed by the Research Corporation and was operated with eminent success. Removal of the accumulations of dust from the precipitator dust bins and contamination of the oil used in the oil-seal system caused some difficulty. As finally evolved, the dust was periodically flushed from the collectors with water, and the seal oil, when contaminated with phosphorus, was purified by treatment with copper sulfate and soda solution. Precipitation of moisture on the precipitator wire insulators caused arcing and severe cracking of the insulators and a forced shutdown to replace them. To prevent recurrence of this difficulty, steam coils were placed in the air compartment surrounding the insulators to heat the air and prevent the condensation of moisture on the insulators.

Temperature control in the condenser proper proved to be very critical. If too much cooling water was used on the external surfaces of the condenser tubes, phosphorus froze within the tubes. This, however, was the only serious difficulty and was remedied by installing a recirculating counter-current cooling water system with a controlled inlet temperature of 110° F.

In successful operation, the heat transfer on the condenser tube surface was 2.5 Btu. per hour per degree Fahrenheit per square foot.

Phosphorus recovery in the tube units amounted to about 70 percent, and the remainder of the phosphorus was entrained as droplets in the gas stream leaving the units. Entrainment of phosphorus is primarily due to rapid cooling which results in fog formation. Also, furnace puffing due to slippage of stock and other reasons blew phosphorus from the surface of the tubes into the exhaust gas line. An entrainment separator of a baffle-wall type was installed in the exhaust line from the condenser and served to collect about 10 to 15 percent of the total phosphorus.

The complete success of the above system of dry condensation of phosphorus depended upon the efficiency of the Nash-Hytor exhaustor pump as an entrainment separator. It collected up to 25 percent of the total phosphorus. As the pump is constructed of corrosion-resistant metal, water is recirculated to it and drains with the phosphorus condensate to the collection tank.

After several years of operation, the following comparisons can be made of phosphorus collection by wet and dry condenser systems: Wet condensers are much more flexible than dry condensers and are less sensitive to fluctuations in furnace operation. Furnace puffs place a greater load on the Nash exhaust pump of the dry system. In the dry system, it is necessary to shut down the entire furnace system to clean condenser tubes or to repair leaks. Dry condenser systems have lower initial and depreciation costs and lower maintenance cost due to the excessive liquor system maintenance cost of the wet systems. Installation of electrostatic precipitators to cleanse gases before condensing phosphorus in wet systems, however, may equalize the maintenance costs of the two kinds of systems. A slightly greater phosphorus recovery has been obtained with the dry system than with the wet system.

Phosphorus, after condensation and collection, is stored usually in underground concrete storage tanks. It is, when necessary, stored in steel tanks above ground, and is shipped in tank cars and tank wagons. Submerged pumps are the most practical method for delivering phosphorus from underground tanks. Where practical, phosphorus is customarily moved from tanks by water displacement so that the pumps handle water rather than phosphorus. Brass lines have proved highly resistant to corrosion from flowing phosphorus. These lines at first were steam jacketed, but present practice is to wrap the lines with steam tracers under insulation. Plugging of lines and attendant difficulties are frequent in the handling of dirty phosphorus. Metering of phosphorus has been very difficult due to its low viscosity in the molten form. In pilot-plant operations, it is delivered by water displacement, and the water flow is metered (13).

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(13) In the discussion of the production of phosphorus in electric furnaces, in addition to direct observation, much of the data presented was gathered in group studies of operating phosphorus units. Additional data may be obtained from published papers, especially those mentioned in footnotes on page 4 of this thesis.

The Properties of Phosphorus

Phosphorus exists in at least four well-recognized modifications. These are usually described by color, and are known as yellow (or white), red, violet, and black phosphorus. All of these probably are not distinctive allotropic forms of phosphorus, as there is considerable support for the belief that the red form may be a physical mixture of white and violet phosphorus. The white allotrope is definitely known. Usually, it is contaminated with at least traces of other allotropes, and is commonly known as yellow phosphorus. Red phosphorus has been known and manufactured for years, but very little progress has been made in improving processes for its production on a very large scale. White phosphorus is altered to red phosphorus by heating under very carefully controlled conditions. Violet and black phosphorus are comparatively stable forms about which little is known. Red, black, and violet phosphorus are progressively more stable than white phosphorus.

A thorough discussion of phosphorus and its principal oxides is presented in standard treatises on chemistry (14).

Some of the thermal properties of phosphorus and phosphorus pentoxide are shown in the following summary:

P_4: Heat of fusion - - - - - - - - - 3.0 Btu. per cu. ft. at 60° F.
Fusion temperature - - - - - - - 111° F.
Heat of vaporization - - - - - 76.5 Btu. per cu. ft. at 60° F.
Boiling temperature - - - - - 535° F.

P_2O_5: Heat of sublimation - - - - - 41.75 Btu. per cu. ft. at 60° F.
Sublimation temperature - - - 680° F.

The heat content of phosphorus and phosphorus pentoxide vapor

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(14) Mellor, J. W. A comprehensive treatment of inorganic and theoretical chemistry. New impression, v 8. N.Y., Longmans-Green, 1940. pp. 771-782.

and the heat contents of other gases involved in phosphorus combustion processes have been calculated from data in the International Critical Tables and various engineering handbooks, and are shown in Figure 1 in a form found convenient for making phosphorus combustion calculations.

The readiness with which phosphorus may be oxidized leads to the fact that it may be burned in the presence of other combustible gases, such as carbon monoxide and hydrogen, without combustion of those gases. Under certain conditions, to be discussed later in this thesis, it may be oxidized with carbon dioxide to produce phosphorus oxides and carbon monoxide, or with water or steam to produce phosphorus oxides and hydrogen.

In effect, therefore, the combustion of phosphorus may be accomplished in three ways: (a) Complete combustion in air. (b) Preferential oxidation in the presence of other combustible gases. (c) Steam or water oxidation.

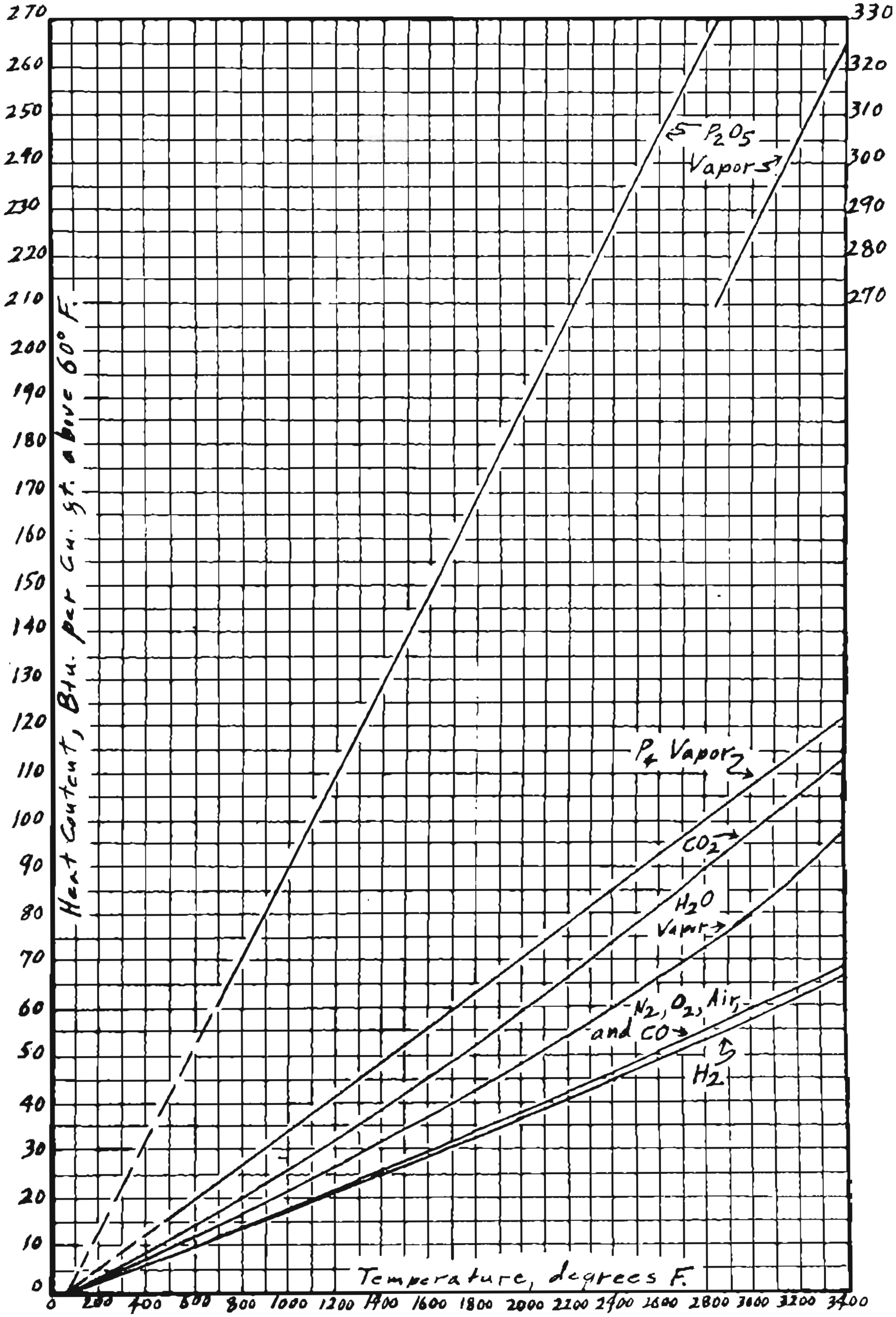

FIGURE 1 – HEAT CONTENT OF GASES FROM PHOSPHORUS COMBUSTION FURNACES

The Combustion of Phosphorus in Air

Phosphorus, in uncondensed form as a product of the electric-furnace reduction of phosphates, is present in a gaseous mixture containing 8 to 8.5 percent phosphorus, 80 to 90 percent carbon monoxide, 1 to 5 percent water vapor, hydrogen, oxygen, and carbon dioxide; certainly at least traces of phosphorus trifluoride and pentafluoride and phosphorus oxyfluoride (POF_3), and probably traces of arsine, phosphine, and various phosphorus oxides.

In present commercial operations, the phosphorus plus other combustibles may be burned completely, or the phosphorus may be condensed, as described in the previous section of this thesis, and burned separately. In either practice, the reaction is the oxidation of phosphorus by oxygen in air.

Phosphorus Ignition: Phosphorus ignites spontaneously in air at normal atmospheric temperatures. Early investigations (15) have shown that the ignition of yellow phosphorus is accelerated by rarification and retarded by compression of the air supplied for the combustion. Under the condition of rarification of the air, a suboxide, the trioxide, the tetroxide, and some red phosphorus may be formed, in addition to phosphorus pentoxide. The writer has detected suboxides of phosphorus in the exhaust gases from phosphorus combustion furnaces operating with an insufficient supply of air for the complete oxidation of phosphorus to phosphorus pentoxide. When phosphorus is burned with an excess of air, it is converted com-

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(15) See footnote 14.

pletely to phosphorus pentoxide.

When a considerable quantity of air at a low temperature is passed over phosphorus, a slow combustion occurs to produce a slight elevation of temperature which gradually accelerates the reaction until the phosphorus finally bursts into flame.

The ignition of phosphorus is accelerated by a great variety of substances, including: ammonium, sodium, and calcium chlorides; antimony and arsenic; barium hydroxide; boric acid; calcium carbonate and lime; charcoal and lampblack; fluorspar; magnesia and manganese; potassium hydroxide; silica; and sodium nitrate. Any conditions which hinder the dissipation of heat generated during oxidation or hasten the rate of oxidation cause phosphorus to ignite.

Zagvozdkin and Barilko (16), recently collected experimental data on the rates of oxidation and the composition of the products formed by the oxidation of phosphorus with atmospheric oxygen at temperatures from 125° to 450° C. They found that a variation of the time of reaction of from 23 to 180 seconds caused only a slight change in the composition of the most of the oxide products, except in the case of P_4O_2 which was formed in comparatively large amount when the oxidation occurred at 125° C. but in lesser amounts when the phosphorus was oxidized at higher temperatures.

The results of these experiments are shown in Table 6:

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(16) Zagvozdkin, K. I., and Barilko, N. A. Rates of oxidation and composition of products in phosphorus oxidation. J. Phys. Chem. (U.S.S.R.) v 14, pp. 505-512 (1940). C. A. v 35, p. 2058.

Table 6

The Relative Amounts of the Oxides of Phosphorus Produced by Burning Phosphorus in Air

Temperature, °C.	Weight percent			
	P_4O_{10}	P_4O_6	P_4O_2	P_4O
125	35	35	4.7 - 0.6	28
250	35	19	0.9 - 4.0	20
350	75	14	0.9 - 0.3	10
450	88	12	0	0

Zagvozdkin and Barilko proposed that their data might be explained by the following equations for the first stage of the oxidation:

1. $P_4 + O = P_4O$
2. $P_4O + O_2 = P_4O_2 + O$
3. $P_4O_2 + O_2 = P_4O_4$

At low pressures, the second stage of the oxidation may be represented by the following equations:

4. $P_4O_4 = 4\ PO$
5. $PO + 2O_2 = PO_2 + O_3$
6. $2\ PO_2 = P_2O_4$
7. $P_2O_4 + O_3 = P_2O_5 + O_2$

At higher pressures, P_4O_4 adds O_2 to produce P_4O_6, P_4O_8, and P_4O_{10}.

Ozone, one of the intermediate products in the oxidation of phosphorus, was also observed by Fishbeck and Eich (17), who stated that it

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(17) Fishbeck, K., and Eich, H. The ozone reaction in the oxidation of phosphorus. Ber. v 71B, pp. 520-532 (1938). C. A. v 32, p. 4414.

is produced by the reaction of phosphorus peroxide with oxygen.

Semonov (18), in an evaluation of numerous earlier investigations, described a critical pressure of oxygen in the oxidation of phosphorus. He showed that this critical pressure, P_k, is related to the partial pressure of phosphorus, P_{P_4}, by the expression, $P_k\sqrt{P_{P_4}}$ equals a constant.

Also, he found that $P_k\{1 + [P_a/(P_k + P_a)]\}$ equals a constant, when another material, a, exerts a partial pressure, P_a.

A valid relationship between the diameter, d, of the reaction tube, and the constant, P_k, is found in the expression, $P_k d^{3/2}$.

This latter relationship is independent of the temperature, except insofar as it affects the partial pressure of phosphorus.

The data of Semonov were reconciled by him with the following concepts relative to the oxidation of phosphorus:

1. The reaction between moles of P_4 and O_2 is not instantaneous.

2. The reacting moles are in an activated state, and may lose their activity by shocks against the walls of the reaction chamber.

3. The reaction is a chain mechanism which proceeds very slowly because of the small number of reaction centers, and could become explosive under certain conditions.

Booy (19) demonstrated the existence of two pressure limits of oxidation of phosphorus, by the aid of the mathematical concept of chain reactions, and found that the pressure limits of oxidation of phosphorus are quite comparable with the explosion limits in explosive gas mixtures.

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(18) Semenov, N. The oxidation of phosphorus vapors at low pressures. J. Phys. Chem. (U.S.S.R.) v 46, pp. 109-131 (1927). C.A. v 22, 901.

(19) Booy, I. J. Explosive gas reactions. Rec. trav. chim. v 49, pp. 866-875 (1930). C.A. v 24, p. 5159.

Melville (20), studied the effect of inert gases in chain reactions, using hydrogen, methane, hydrogen sulfide, carbon disulfide, phosphine, and phosphorus. He found that the inert gases accelerate the oxidation of the lighter molecules more than that of the heavier molecules, and that the velocity of the chain reaction is inversely proportional to the diffusion coefficient of the chain through the gas mixture.

King and Ludlam (21), in studying the chain theory of oxidation of phosphorus vapor, found that deuterium and helium are almost equivalent in their capacity to prevent the explosion chain carriers from reaching the walls of the reaction chamber, and that hydrogen is less efficient. The ratios for the retarding effect are: $H_2:D_2:He = 1.00:1.30:1.32$. They found that illumination of the gas mixture with ultraviolet light, from a zinc spark or a mercury arc, below the lower explosion limit, (a) displaced the lower limit to lower pressures and (b) induced reaction between phosphorus and oxygen below this limit. The displacement is a wall effect, probably due in the first place to dissociation of P_4 to P_2. The displacement is not permanent, but slowly decays as the reaction mixture is allowed to stand before being exploded. Ultraviolet light raised the upper explosion limit. As this could not be explained as a wall effect, it was interpreted as resulting from the production of P_2 molecules. The rate of the stable reaction is proportional to the pressure of P_4 and to the square of

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(20) Melville, H. W. Inert gas effects in chain reactions. Trans. Faraday Soc. v 28, pp. 814-818 (1932).

(21) King, D. W., and Ludlam, E. B. Chain theory of the oxidation of phosphorus vapor. J. Chem. Soc. Part II, pp. 1500-1503 (1938).

the oxygen pressure, although independent of the pressure of the inert gas.

The foregoing general concepts of phosphorus oxidation will be elaborated later in the discussion of special cases of oxidation, i.e., preferential oxidation and oxidation with water.

For the present discussion of phosphorus combustion in air, it is important only that the following requirements be established:

(1) Phosphorus is burned almost completely to phosphorus pentoxide (P_4O_{10}) in the vapor state, only in the presence of excess air.

(2) Phosphorus combustion in air is a slow chain reaction and ample combustion space must be provided for completion of the reactions.

(3) Phosphorus is burned best when it has been vaporized prior to combustion.

Industrial Phosphorus Burners

Two important industrial processes utilize phosphorus combustion as an essential item in their operation, i.e., the manufacture of phosphoric acid and the manufacture of the metaphosphates.

Prior to the elucidation of the principles involved in the combustion of phosphorus, many trials were made of various kinds of phosphorus burners. These were mostly based on the belief that, inasmuch as phosphorus may be handled in the liquid state in much the same way as fuel oil or other liquid fuel, it might readily be handled in a liquid-fuel burner. Most early attempts at burning phosphorus without prevaporization were failures. It was found that the phosphorus, usually containing water and other impurities, is highly corrosive to metals and that metallic burner tips are rapidly corroded away.

Water-cooling of the burner nozzles failed to afford much relief, and a burner designed so that secondary combustion air cooled the nozzle was not much more successful. However, in spite of the fact that burner nozzles are corroded and must be frequently replaced in service, they are used in pilot-plant installations and elsewhere when their short life is not a very great economic factor. In these instances, they are simple, inexpensive, nipple-type burners.

The most notable advance in phosphorus burning came about when it was accepted that phosphorus should be vaporized preliminary to ignition.

Three patents granted to individuals who have been intimately associated with the solution of the problem of burning phosphorus are abstracted below to show how the problem is handled:

Phosphorus vaporizer (22)

Liquified phosphorus is introduced into a confined zone and continuously vaporized, thoroughly mixed with excess air over that required for complete oxidation. The proportion of phosphorus vapors to air is controlled by regulating the temperature of the liquid phosphorus, as by externally heating the vessel in which it is contained.

Oxidizing phosphorus (23)

A primary air supply is used sufficient to vaporize all of the phosphorus and sufficient to oxidize only a limited amount of the phosphorus. A secondary air supply is used in amount sufficient to

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(22) Zinn, R. E. Phosphorus vaporizer. U. S. patent 1,991,916. Assigned to Victor Chemical Company (1935).

(23) Junkins, J. N. Oxidizing phosphorus. U. S. patent 2,125,297. Assigned to the Tennessee Valley Authority (1938).

convert all of the partly oxidized and unoxidized phosphorus to phosphorus pentoxide, and to form a hot gaseous mixture containing the latter. The operation of the process comprises introducing the phosphorus into an uncovered liquid-confining zone substantially centrally located in a surrounding gas-confining zone, passing the primary air in heat-exchange relationship with the hot gaseous mixture containing phosphorus pentoxide. The heated primary air is admitted to the gas-confining zone immediately above the surface of the phosphorus contained in the liquid-confining zone to form a gaseous mixture of partly oxidized and unoxidized phosphorus. The secondary air is admitted to the gas-confining zone so that it will be mixed with the gaseous mixture of partly oxidized and unoxidized phosphorus to form the hot gaseous mixture containing phosphorus pentoxide which is passed in heat-exchange relationships to both the primary air and the liquid-confining zone.

The oxidation of crude phosphorus (24)

The process comprises treating crude phosphorus containing solid impurities in a vaporizing chamber containing an atmosphere of vapors of phosphorus and oxidized phosphorus. The crude phosphorus and air are continuously injected into the chamber, while maintaining the quantity of air supplied at such an amount that the oxygen content is only a minor part of the amount theoretically required for complete oxidation of all of the phosphorus. The amount of air used is sufficient to maintain the temperature of the partly oxidized combustion products above the fusion point of the solid impurities associated therewith, of the order of 900° to 1100° C.

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(24) Almond, L. H. The oxidation of crude phosphorus. U. S. patent 2,221,770. Assigned to the Tennessee Valley Authority (1940).

Industrial Processes Utilizing Phosphorus Combustion

The combustion of phosphorus to produce useful products is best exemplified in the phosphate fertilizer industry and by the engineering developments of the Tennessee Valley Authority. The publications that are cited below trace the development of the electric-furnace method for producing phosphoric acid and concentrated superphosphate (25), calcium metaphosphate (26), and potassium metaphosphate (27).

As is shown by Figure 2, the combustion of phosphorus in air is the starting point for manufacturing each of the aforementioned materials. This composite scheme of manufacturing phosphate fertilizers represents the status of phosphates production processes at the Wilson Dam plant of the Tennessee Valley Authority. One process for manufacturing concentrated superphosphate and two processes for manufacturing calcium metaphosphate have been in operation in full-scale plant units for several years. A process for manufacturing potassium metaphosphate has been operated on large pilot-plant scale for several years.

Phosphoric Acid Manufacture: The production of phosphoric acid, as a separate operation, is required only for the production of concentrated superphosphate, a product of reaction of the acid with rock

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(25) Curtis, H. A. General Outline of activities. Tennessee Valley Authority, Department of Chemical Engineering. Chemical Engineering Report No. 1. Treasurer's Office, Tennessee Valley Authority, Knoxville, Tennessee (1940). Also see footnotes 2-9.

(26) Curtis, H. A., Copson, R. L., and Abrams, A. J. Metaphosphate investigations aim at cheaper fertilizers. Chem. Met. Eng. v 44, pp. 140-142 (1937), and Manufacture of calcium metaphosphate in a full-scale unit. Trans. Am. Inst. Chem. Engrs. v 34, pp. 287-313 (1938).

(27) Copson, R. L., Pole, G. R., and Baskervill, W. H. Development of processes for metaphosphate productions. Ind. Eng. Chem. v 34, pp. 26-32 (1942).

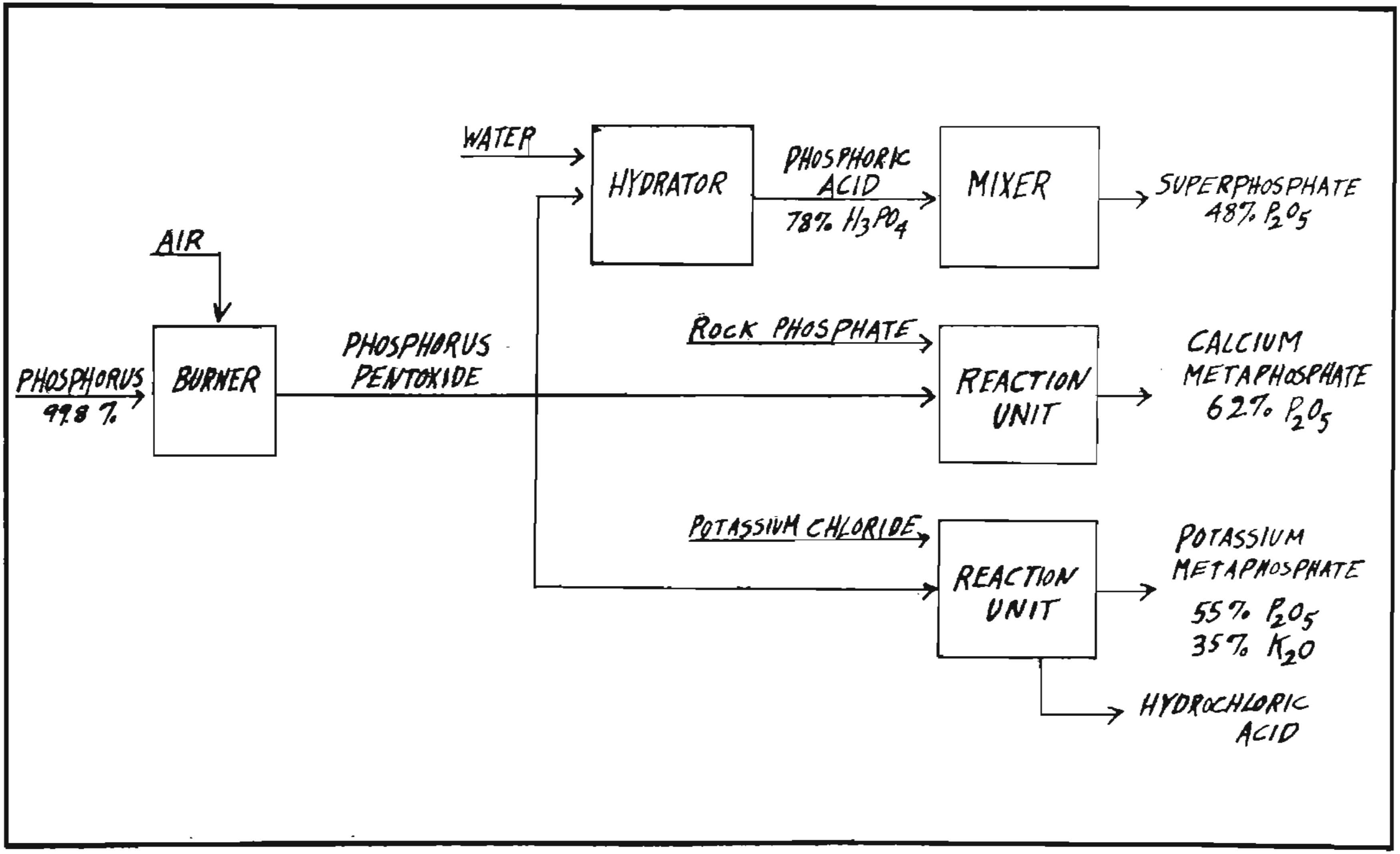

FIGURE 2 — PHOSPHATE FERTILIZERS MADE BY PHOSPHORUS COMBUSTION PROCESSES

phosphate. Beyond this, however, orthophosphoric acid and similar acids of phosphorus are likely to become increasingly important as industrial acids. Among the new applications of phosphoric acid is its use as a dehydrating agent in the production of nitrocellulose by nitration of cotton linters. Recent research on the production of phosphoric acids is described in published papers (28).

Various processes for the production of phosphoric acid by burning phosphorus and absorbing the phosphorus pentoxide product in water or in acid have been applied on a large-plant scale at Wilson Dam.

A description of a typical process for the production of phosphoric acid is as follows: Liquid phosphorus flows into a horizontal, refractory-lined vaporizer. A small proportion of the total quantity of air required to burn the phosphorus is admitted to the vaporizer, wherein just sufficient phosphorus is burned to supply the heat to vaporize the remainder of the phosphorus. The stream of vaporized phosphorus, phosphorus oxides, and nitrogen arises from one end of the combustion chamber, through a metal duct. A reverse turn at the upper end of the duct permits delivery of the vapor stream into the top of a large, cylindrical, horizontal phosphorus burner. Here, sufficient increment of ai~~t~~ is provided to complete the combustion of the phosphorus to phosphorus pentoxide. The

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(28) Baskervill, W. H. The packed-tower collection of phosphoric acid. Trans. Am. Inst. Chem. Engrs. v 37, pp. 79-94 (1941).
Walthall, J. H., and Striplin, M. M. Superphosphoric acid by absorption of phosphorus pentoxide vapor. Ind. Eng. Chem. v 33, pp. 995-1000 (1941).

resultant gas stream, consisting of phosphorus pentoxide, nitrogen, and oxygen, flows through another duct into a hydrator where it ascends through water mist descending from sprays. Acid formed and condensed in this unit falls to the bottom and is drained from the hydrator tower into an acid-collecting sump. Much of the acid, however, is not collected in the hydrator, and ascends in the form of mist to the top of the tower, from which it is withdrawn through a duct and through an electrostatic precipitator by an exhaust fan. The remainder of the acid in the gas stream is precipitated in the precipitator and then flows into the sump that delivers the acid to storage tanks.

Variations of the scheme described above are the combination of the burner and hydrator units in a single tower and the substitution of a coke-packed tower for the electrostatic precipitator.

Concentrated Superphosphate Manufacture: Concentrated superphosphate (a material containing about 48 percent phosphorus pentoxide, as compared with ordinary superphosphate containing about 16 percent phosphorus pentoxide) is produced by the reaction of phosphoric acid with rock phosphate. Various details of the processes developed by the Tennessee Valley Authority have been described (29).

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(29) See footnotes 3, 4, and 5.
Copson, R. L., Newton, R. H., and Lindsay, J. D. Initial reaction rate between phosphate rock and phosphoric acid. Ind. Eng. Chem. v 29, pp. 175-179. (1937).
Hardin, L. J., Oldham, F. D., and Hammond, J. W. Development of P_2O_5 insolubility in phosphate mixtures: The formation of fluorapatite and its cause. Ind. Eng. Chem. v 29, pp. 758-766 (1937).

A brief description of the operations of manufacturing concentrated superphosphate is as follows: Acid from the acid plant (80 to 90 percent H_3PO_4) is pumped to yard storage tanks or to tanks in the superphosphate building, where it is diluted with water or with weak acid to the desired concentration of 78 percent H_3PO_4. Rock phosphate is unloaded from railway cars on a trestle by an inclined conveyor belt, or, if the material is dry and less than 1/4 inch mesh size, by a Dracco pneumatic unloading system. The rock is dried if necessary, and is ground in Raymond mills to a fineness of approximately 50 percent through a 325-mesh sieve. The ground rock is transferred from the mills to silos in the manufacturing building by a Holley pneumatic conveyor system.

Phosphoric acid is mixed with the rock dust in two batch mixers. The mixers are of the sigma-blade type, manufactured by the Read Machinery Company, and each one handles 1200 pounds of rock phosphate and produces a mix of green superphosphate every 10 minutes. The actual mixing requires only 1-1/2 minutes and the balance of the time is used for loading and unloading the mixer. The ratio of acid to rock used for the mixture is varied and amounts to from 80 to 95 percent of the amount of phosphoric acid required to react with the CaO, P_2O_5, Fe_2O_3, and Al_2O_3 in the rock. The exact ratio of acid for each kind of rock phosphate is determined by the application of a mathematical formula taking into account the relative costs of the materials and the properties of the product. Obviously, the acid is the most expensive material, and the least amount of acid required to give a satisfactory product is the amount used to produce the superphosphate.

The superphosphate leaves the mixers in the form of moist, pulverant lumps dropped on a conveyor belt which transports it to trolley cars running on a monorail track circumscribing the inside eaves of a storage building. The superphosphate is dumped from the trolley cars into bays in the storage building where it is permitted to cure in piles for a period of 8 to 12 weeks. Preliminary studies of accelerated curing processes were successful, but additional handling costs are undesirable. The curing operation decreases free acid and insoluble phosphate contents of the product, or, in other words, increases the conversion of the phosphate from the rock phosphate into soluble or "available" form.

Cured superphosphate is taken from the piles by grab-bucket tractor cranes, and dropped through a grizzly onto a belt conveyor which carries it to the superphosphate preparation building. It is then ground in a squirrel-cage disintegrator, bagged in 100-pound bags, and shipped.

Concentrated superphosphate has the characteristics shown in Table 7:

Table 7

The Characteristics of Concentrated Superphosphate

Chemical Analysis:

		P_2O_5				
	Moisture	Total	Available	Free acid	Insoluble	CaO
Before curing	-	48.9	47.1	4.9	1.8	21.2
After curing	3.1	49.7	48.2	1.2	1.5	22.1

Sieve Size:

	Cumulative percent through		
	4 mesh	10 mesh	20 mesh
As shipped	99.0	78.3	64.9

Calcium Metaphosphate Manufacture: Unlike concentrated superphosphate, calcium metaphosphate has not yet reached the status of wide acceptance as a fertilizer material. Its definite advantage as a fertilizer is due to its very high content of phosphorus in available form — approximately 65 percent phosphorus pentoxide.

Calcium metaphosphate, as a fertilizer material, is the product of research and engineering development by the Tennessee Valley Authority (30). Various processes have been devised and are being developed to improve the methods for the production of the metaphosphate. Design, operating, and economic data on one of these processes has been published (31).

Natural lump rock phosphate or agglomerated phosphate fines are delivered by a skip hoist to the top of a reaction tower, and are charged through a feed hopper into the tower where they rest on refractory grates. The grates are internally cooled by a flowing stream of water or air. Phosphorus is burned with air in a combustion chamber immediately below the grates sustaining the burden of rock phosphate. The hot gases from the burning phosphorus ascend through the rock burden and by their stored heat content initiate and sustain the reaction of phosphorus pentoxide with rock phosphate to form calcium metaphosphate;

$$Ca_3(PO_4)_2 + 2 P_2O_5 = 3 CaP_2O_6.$$

The calcium metaphosphate, in a fused state, flows from the grates of the tower into the base of the combustion chamber from which it is periodically tapped. The fluid metaphosphate, on tapping, flows into a rotary cooler (externally cooled by water from sprays) where it first

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(30) See footnotes 25, 26, and 27.

(31) See footnote 26.

cools in a thin film and then breaks free from the wall of the cooler due to the contraction on cooling. The flakelike lumps of calcium metaphosphate are disintegrated, usually in a cage mill, and bagged in the same way as concentrated superphosphate.

It is expected that better methods will be developed for the manufacture of calcium metaphosphate, as very definite objections to the above scheme have been found during several years of operation of a unit, like the above, producing nearly 50 tons of calcium metaphosphate per day. Probably the most serious difficulty with the described process is the rapid corrosion and failure of the refractory grates used to sustain the lump phosphate burden. "Corhart" (high alumina, electrocast) refractory shapes were used for the construction of the grates and suffered severe corrosion. In present practice, these refractories are faced with zircon blocks. The zircon refractory, although very expensive, apparently is the only material that will resist for any time the attack of the corrosive gases and molten metaphosphate.

Another process for manufacturing calcium metaphosphate, now being developed, uses rock phosphate fines which are blown with air directly into the phosphorus combustion chamber. This process has shown some promise, but has also created new difficulties. The reaction chamber for the phosphate fines process must be surmounted by a coke-filled tower. The packing of this tower is continually wetted by water or recirculated phosphoric acid from sprays to collect and absorb phosphorus pentoxide produced by the burning phosphorus. The acids drip from the absorption tower onto the pile of rock phosphate fines blown into the furnace. This operation is necessary to provide the proper time of contact between rock phosphate particles and the gaseous products of phosphorus combustion. The major difficulty in the fines process is the necessity for handling and circulating a hot phosphoric acid medium. This acid contains fluorine from the rock phosphate and is extremely corrosive. Research is in progress to remove fluorine from the acid, in a continuous operation, and thus decrease acid corrosion to reasonable limits.

Inasmuch as research and development is continuing and processes for the production of calcium metaphosphate have not yet attained a state of complete commercial success, a more detailed discussion cannot be given at this time.

Potassium Metaphosphate Manufacture: Potassium metaphosphate can be manufactured by processes similar to those for calcium metaphosphate. Pilot-plant development has indicated that a process similar to the previously mentioned fines process is probably the most desirable one. In making potassium metaphosphate by the process, potassium chloride is blown with air into the phosphorus combustion chamber and converted into metaphosphate by the following reaction:

$$2\ KCl + H_2O + P_2O_5 = 2\ KPO_3 + 2\ HCl.$$

A tower filled with coke packing is also used in this process to collect and return phosphorus, in the form of phosphoric acid, to the reaction zone. The hydrochloric acid vapor, due to its greater volatility, is drawn from the top of the absorber tower, condensed by cooling, and drawn through a limestone-filled tower to neutralize it. Present research is in progress to determine methods for the utilization of the hydrochloric acid byproduct of the process. One of the most promising methods is to use it to react with rock phosphate to produce dicalcium phosphate. This application is still in a pioneering stage of development.

The value of potassium metaphosphate lies in the fact that it contains both phosphorus and potassium in highly concentrated forms directly available as fertilizers.

Fertilizers from Phosphorus: The foregoing brief description of the development of processes by the Tennessee Valley Authority is supplied in explanation of Figure 2, which aims to show the relation of phosphorus combustion in air to the development of fertilizer processes.

Not all the of the fertilizer materials mentioned above have reached the status of unqualified acceptance by agriculture, but definite advances in this direction have been made within recent years. Agricultural experiment stations throughout the United States and its possessions are making extensive tests, and a considerable tonnage of the fertilizers have been distributed to farmers for trial under diverse agricultural conditions. A resume of the manufacturing and distribution data, complete through the year 1941, is shown in Table 8. Normal development of fertilizer manufacturing processes has been prevented, since 1941, due to the tremendous demand for munitions phosphorus.

Table 8

Production and Distribution of Fertilizer by TVA (32)

(Net tons for fiscal years ending June 30 of year indicated)

Production	1935	1936	1937	1938	1939	1940	1941
Superphosphate	19,884	27,028	35,012	47,268	67,698	79,089	96,373
Metaphosphate	-	-	-	4,514	4,647	3,798	11,447
Distribution							
Superphosphate:							
to demonstration farms	2,209	29,806	22,644	13,464	14,438	20,115	18,619
to A.A.A.	-	-	17,119	26,250	50,480	62,324	68,021
to other agencies	-	88	26	44	43	70	351
Total	2,209	29,894	39,789	39,758	64,961	82,509	86,991
Metaphosphate:							
to demonstration farms	-	-	-	414	3,867	7,901	9,254

The results of practical tests of the fertilizer materials have been favorable. Except in cases where the calcium sulfate content of ordinary superphosphate is a distinct advantage to a particular type of soil or crop, the TVA fertilizers have been found to be as efficient forms as any of the older fertilizer materials.

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(32) See footnote 25.

The Preferential Oxidation of Phosphorus

Phosphorus and carbon monoxide, when burned with an excess of oxygen, are each capable of burning under contions wherein a theoretical flame temperature of above 2000° C. is reached. This condition of complete combustion may be expressed by the following equations:

$$P_4 + 5\ O_2 = P_4O_{10} + 1{,}316{,}720\ \text{Btu.}$$

$$10\ CO + 5\ O_2 = 10\ CO_2 + 1{,}226{,}400\ \text{Btu.}$$

It is apparent that if a gas containing 1 mole of P_4 and 10 moles of CO is burned, nearly 50 percent of the total heat is not useful heat, i. e., not heat evolved in the useful reaction of the oxidation of P_4 to P_4O_{10}.

The fact that under certain conditions carbon dioxide, produced by the combustion of carbon monoxide, may in turn serve to oxidize phosphorus and be reduced back to carbon monoxide was ascertained by numerous investigators. Klugh (33), in 1923, obtained a patent in which he stated that the phosphate material is electric smelted together with a siliceous flux and carbon or other reducing material to produce carbon monoxide and phosphorus, and that these gases are treated with a restricted amount of air to oxidize the phosphorus without appreciable oxidation of the carbon monoxide.

Britzke, at about the same time, also obtained a patent for preferential oxidation of phosphorus (34)which states that in producing

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(33) Klugh, B. G. Electric furnace oxidation of phosphorus. U. S. patent 1,463,959 (1923).

(34) Britzke, E. Power gas and phosphorus. Brit. patent 229,768 (1923).

phosphoric acid by treatment of phosphates with silicates and carbon in a shaft furnace, the oxidation of the phosphorus present in the evolved gases is effected with air or oxygen at a temperature of 1000° to 1300° C. so that substantially no oxidation of carbon monoxide occurs.

Emmett and Shultz (35), in 1939, performed experimental work to establish the characteristics of the $CO-CO_2-P_2O_4-P_2O_5$ equilibrium. They found that in the temperature range of 800° to 1200° C., a gaseous mixture of phosphorus and carbon dioxide, containing more than 11.1 percent phosphorus vapor, quickly reaches equilibrium corresponding to the conversion of about 80 percent of the carbon dioxide to carbon monoxide. If less than 11.1 percent phosphorus was present, practically all of the phosphorus is absent in the equilibrium mixture at these temperatures, and a mixture of phosphorus pentoxide and phosphorus tetroxide is obtained. The equilibrium in the system is such that with equal molal quantities of the pentoxide and tetroxide, the ratio of carbon monoxide to carbon dioxide is about 1 to 2. It was also shown that, in the presence of rock phosphate to absorb the phosphorus pentoxide as formed, the oxidation of phosphorus by carbon dioxide is complete, and the phosphate product formed is calcium metaphosphate.

The Tennessee Valley Authority, previous to the work of Emmett and Shultz, had undertaken work on the production of calcium metaphos-

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(35) Emmett, P. H., and Shultz, J. F. Oxidation of phosphorus to a pentavalent form by carbon dioxide. Ind. Eng. Chem. v 31, pp. 105-111 (1939).

phate, and was also interested in the possibilities of the utilization of preferential oxidation in processes for manufacturing phosphoric acid directly from gases containing phosphorus and carbon monoxide, without burning the carbon monoxide. Curtis of the TVA recognized that phosphorus blast-furnace gas could be used in the stoves to preheat the air blast if the phosphorus in the furnace exhaust gas could be oxidized to phosphorus pentoxide without burning the carbon monoxide to carbon dioxide (36).

Frear, Ogg, and Hull (37) of the TVA have prepared data collected after several months of small-scale and pilot-plant work. Almost complete oxidation of phosphorus was accomplished at temperatures of 500° to 700° C., with the oxidation of about 1 percent of the carbon monoxide, using about 160 percent of the air theoretically required for the oxidation of phosphorus to the pentoxide, and a gas mixture containing 1 percent phosphorus and 39 percent carbon monoxide. Preferential oxidation at 1100° C. was found possible with this gas mixture when the phosphorus pentoxide produced was reacted with rock phosphate to produce calcium metaphosphate.

A narrower temperature range, 550° to 600° C., and less excess air, 125 percent of the theoretical, favored the preferential oxidation when the gas mixture consisted of 7 percent phosphorus and 90 percent carbon monoxide. Under the latter conditions, the oxidation of the phosphorus was substantially complete, and 2 percent of the carbon monoxide was oxidized to carbon dioxide. The presence of water vapor increased the

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(36) See footnote 25.

(37) Frear, G. L., Ogg, E. R., and Hull, L. H. The preferential oxidation of phosphorus in the presence of carbon monoxide. (In preparation).

oxidation of carbon monoxide, and the combustion rates required careful control, with both gas compositions. The two gas mixtures studied by the TVA simulated phosphorus blast furnace and electric furnace gas, respectively.

Having demonstrated the actual workability of preferential oxidation for gases from either the blast or the electric furnace, the TVA evaluated its findings as follows:

The air for combustion may be dry or it may contain sufficient water vapor to convert the pentoxide into metaphosphoric acid. The combustion rate should be 0.3 pound of phosphorus per hour per cubic foot of combustion space. By lowering the temperature, drying the air, and decreasing the proportion of air to combustibles, the actual amount of carbon monoxide as well as its concentration may be increased in the furnace exhaust gas, thus increasing the heating value of this gas and decreasing the dilution of phosphorus pentoxide contained therein. However, the richest exit gases produced from the simulated blast-furnace gas and electric-furnace gas contained 30 percent and 34 percent, respectively, of carbon monoxide, due to the dilution by nitrogen. This gas composition has a heating value of about 100 Btu. per cubic foot, or approximately the same as for the gas from the iron blast furnace.

The Reactions of Phosphorus with Water

Mellor (38) reviews the data obtained by a number of early investigators who show that water can be decomposed by phosphorus. L. Gmelin and B. von Dybkowsky showed that phosphorus and water can react chemically at ordinary temperatures, and C. F. Gross and A. Higgin found that the reaction occurs only in the presence of oxygen. T. Weyl observed that phosphorus decomposes warm water with the evolution of phosphine. V. Ipatieff and V. Nikolaieff stated that white phosphorus and water in a sealed tube at 360° C. yield phosphoric acid and phosphine, and that the formation of phosphine starts at about 290° C. and 40 to 50 atmospheres pressure, as indicated by a break in the temperature-pressure curve.

Russian research workers have been particularly active in exploring the mechanism of phosphorus decomposition by water. Kureodov and others (39) obtained a patent in 1931 for a continuously operated autoclave for oxidizing phosphorus. Their apparatus consisted of an external thick walled jacket and an inner cylinder surrounded by water. The inner cylinder was divided into an upper reaction chamber and a lower chamber subdivided by plates with overflow tubes. The upper chamber was provided with a tube for the admission of liquid phosphorus and water, terminating in a mixing nozzle. A tube was provided for the transfer of the reaction liquid into the lower chamber and another tube for the escape of the gaseous reaction products.

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(38) See footnote 14.

(39) Kureodov, A. M., Ignatyuk, V. G., and Drennov, K. A. A continuously operated autoclave for the oxidation of phosphorus. Russian patent 27,381 (1931). C. A. v 27, p. 2258.

Frost and others reported on the results of experiments relative to the water oxidation of phosphorus, and proposed formulas for the reactions that they observed:

The oxidation of yellow phosphorus with water at elevated temperature and pressure (40)

The oxidation of yellow phosphorus proceeds at the same velocity as that of red phosphorus, although the phosphoric acid produced by the oxidation of yellow phosphorus is more nearly pure, and the hydrogen is more contaminated with phosphine and phosphorus vapors, than when red phosphorus is oxidized. Atomized phosphorus and water were pumped into the reaction vessel, with the injection nozzle protected from excessive heating to avoid the formation of red phosphorus. A catalyst consisting of sodium hydroxide was admitted separately in the form of a cold concentrated solution. The reaction vessel was fitted with partitions to retard the passage of the reaction mixture. The vessel was heated by stages. After an initial preheat to 325° C., further heating was provided by the reaction. The highest yield of phosphoric acid was obtained when the pressure on the mixture was sufficient to maintain the reagents in the liquid phase.

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(40) Bushmakin, I. N., Ruisakov, M. V., and Frost, A. V. The oxidation of yellow phosphorus with water at elevated temperature and pressure. J. Applied Chem. (U.S.S.R.) v 6, pp. 588-606 (1933). C. A. v 28, p. 3678.

The oxidation of red phosphorus with water at elevated temperature and pressure (41)

As a result of experiments carried out in a silver-lined autoclave, heated in a molten metal bath, Frost explained the oxidation of red phosphorus by water using the following equations:

1. $P_4 + 6 H_2O = 2 H_3PO_3 + 2 PH_3$
2. $P_4 + 8 H_2O = 2 H_3PO_4 + 2 PH_3 + 2 H_2$
3. $P_4 + 12 H_2O = 4 H_3PO_3 + 6 H_2$
4. $P_4 + 16 H_2O = 4 H_3PO_4 + 10 H_2$

He assumed that the intermediate products, H_3PO_3 and PH_3, may react as follows:

5. $H_3PO_3 + H_2O = H_3PO_4 + H_2$
6. $4 H_3PO_3 = 3 H_3PO_4 + PH_3$
7. $PH_3 + 3 H_2O = H_3PO_3 + 3 H_2$
8. $PH_3 + 4 H_2O = H_3PO_4 + 4 H_2$

The process takes place in two stages. In the first stage, the phosphorus is dissolved according to reactions 1 to 4. In the second stage, the intermediate products are oxidized according to reactions 5 to 8. An almost complete conversion of phosphorus to phosphoric acid and hydrogen was obtained by heating to 400° C. without a catalyst. In the presence of 1 percent NiO, the reaction was completed in 4 minutes, at 280° C., and the liquid phase contained 20 to 25 percent of the total phosphorus as H_3PO_4. The catalyst affected only the first stage of the reaction. The maximum yield was obtained when the ratio of water to phosphorus was 3. The partial

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(41) Bushmakin, I. N., Ruisakov, M. V., and Frost, A. V. The oxidation of red phosphorus with water at elevated temperature and pressure. J. Applied Chem. (U.S.S.R.) v 6, pp. 577-587 (1933). C. A. v 28, p. 3678.

pressure of hydrogen had no apparent effect on the velocity of the reaction within the range of 35 and 100 atmospheres.

The two following patents deserve to be mentioned with relation to the nature of other catalysts used for the acceleration of the reactions of phosphorus with water: (1) A French patent (42) makes the statement that phosphides, particularly those of copper and nickel, are used as catalysts for the oxidation of phosphorus by water. The phosphides are prepared by the reaction of phosphine with metallic salts distributed or suitably supported on calcined bone, coke or porous blocks of silicon carbide, ferrosilicon, etc. (2) Miner (43) states that the reaction of phosphorus with water is effected in the presence of an alkali metal such as potassium intermixed with phosphorus in the form of a condensate.

Ipatiev and Usachev (44) found that the oxidation of phosphorus with water vapor under pressure, in the presence of 1.00 to 9.75 N. NaOH solution, produces various oxidation products. They found that if enough NaOH is used to form Na_2HPO_3, only H_3PO_3 is obtained at temperatures not higher than 225° C., while H_3PO_4 is obtained at temperatures of above 250° C. The sodium salt of H_3PO_2 can be oxidized

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(42) Compagnie Nationale De Matieres Colorantes Et Manufactures De Produits Chimiques Du Nord Reunies, Etablissements Kuhlmann. French patent 635,501 (1927). C. A. v 22, p. 4738.

(43) Miner, C. G. Oxy-compounds of phosphorus. U. S. patent 1,686,873 (1928).

(44) Ipatiev, V. N., and Usachev, P. V. Oxidation of phosphorus with water at high temperatures and pressures in the presence of alkalies. J. Am. Chem. Soc. v 57, pp. 300-302 (1935).

completely to H_3PO_3 or H_3PO_4 (without the evolution of PH_3), depending upon the amount of NaOH used and the temperature.

Ipatiev and Freitag (45) explained the oxidation of phosphorus by water at elevated temperatures and pressures by the following equations:

1\. $P_4 + (3 + n)\ H_2O = P_2O_3.nH_2O + 2\ PH_3$

2\. $P_2O_3.nH_2O + 2\ H_2O = P_2O_5.nH_2O + 2\ H_2$

3\. $2\ PH_3 + (5 + n)\ H_2O = P_2O_5.nH_2O + 8\ H_2$

Over a period of considerable time, they found that only phosphoric acid and hydrogen are formed:

4\. $P_4 + (10 + 2n)\ H_2O = 2\ P_2O_5.nH_2O + 10\ H_2$.

The effects of variables were studied between 175° and 420° C. and between 20 and 530 atmospheres pressure. The velocities of all of the reactions increased with higher temperature. In the absence of catalysts, temperatures of about 280° C. and higher were essential for the oxidation of P_2O_3, the first reaction being the most rapid. Metallic salts, especially those of nickel and cobalt, but also silver, copper, and iron, showed marked catalytic activity. Small quantities of nickel nitrate made the reaction go to completion in a short time, at 200° C.

A French patent (46) states that phosphorus is oxidized by water vapor either mixed or not mixed with air, in the presence of binary, tertiary, or quarternary metallic compounds of silicon, such as silicides of copper, double silicides of nickel and copper, or triple silicides of iron, copper, and nickel.

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(45) Ipatiev, V. N., and Freitag, C. Oxidation of phosphorus with water at elevated temperatures and pressures. Z. anorg. allgem. Chem. v 215, pp. 388-414 (1933). C. A. v 28, p. 1594.

(46) Compagnie Nationale De Matieres Colorantes Et Manufactures De Produits Chimiques Du Nord Reunies, Etablissements Kuhlmann. The oxidation of phosphorus. French patent 635,432 (1927). C. A. v 24, p. 697.

The Oxidation of Phosphorus with Steam

Based on the investigations of the reactions of phosphorus with water, considerable interest now exists relative to the possible development of practical processes for oxidizing phosphorus with steam. Conceivably, a process might be evolved using equipment similar to that used in the production of calcium metaphosphate and producing hydrogen gas as well as the metaphosphate.

Liljenroth (47) obtained a patent on a process for oxidizing phosphorus with steam at a temperature of 1000° C. Brunauer and Shultz (48) investigated the reaction in the presence and absence of rock phosphate. The latter investigators concluded that when phosphorus is oxidized by steam at 1000° to 1100° C., the products of the reaction are not merely phosphorus pentoxide and hydrogen, but also phosphorus tetroxide and phosphine. Since compounds of the lower oxides of phosphorus are harmful to plants, these must be eliminated if the oxidized phosphorus is to be used for the manufacture of fertilizers. If the hydrogen is to be used for the synthesis of ammonia, the phosphine must be removed as it poisons ammonia-synthesis catalysts. Both of these undesirable products are eliminated if the reaction of phosphorus with steam occurs in the presence of rock phosphate; the tetroxide is oxidized to pentoxide, which in turn reacts with the rock phosphate to give calcium metaphosphate, and the

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(47) Liljenroth, F. G. Oxidizing phosphorus. Canadian patent 247,164 (1925); U. S. patents 1,594,372 (1926) and 1,673,691 (1928).

(48) Brunauer, S., and Shultz, J. F. The oxidation of phosphorus by steam. Ind. Eng. Chem. v 33, pp. 828-832 (1941).

hydrogen becomes free of phosphine.

These findings of Brunauer and Shultz appeared to indicate that the process might be a successful one, and research was undertaken. The heat requirement of the process appear to be excessively high for the direct application of steam oxidation of phosphorus in furnaces of present design.

An approximation of the additional heat required for the oxidation of phosphorus by steam in a calcium metaphosphate furnace was prepared by the author of this thesis, and is shown in Table 9. In this table, a heat balance for a calcium metaphosphate furnace using air for the combustion of phosphorus (49) is compared with a similar balance that would be effective if a mixture of air and steam were substituted for air alone.

In making the substitution, it was assumed that the mixture of air and steam would be exactly proportioned to give an exhaust gas from the furnace containing 3 moles of hydrogen for each mole of nitrogen, and thus result in an exhaust gas mixture suitable for the synthesis of ammonia.

The datum temperature for the heat balances was 32° F. A value of 79 percent excess air was assumed when air alone was used for the combustion of phosphorus, and a value of 150 percent excess air when the mixture of air and steam was used. The temperature in the combustion chamber was 1960° F.

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(49) Curtis, H. A., Copson, R. L., Abrams, A. J., and Junkins, J. N. Full-scale production of metaphosphate achieved at Wilson Dam. Chem. Met. Eng. v 45, pp. 318-322 (1938).

Table 9

Comparative Heat Balances when Burning Phosphorus with Air and with a Mixture of Air and Steam in a Metaphosphate Furnace

	Air oxidation		Air + steam oxidation	
Input:	Ton moles	Btu. x 10^6	Ton moles	Btu. x 10^6
P_4 at 167° F.	6.2	0.5	6.2	0.5
H_2O at 167° F.	2.7	0.7	2.7	0.7
Air at 80° F.: N_2	47.4	1.16	4.0	0.1
O_2	14.2	0.34	1.18	0.03
H_2O	0.6	1.3	19.2	44.7
Rock phosphate at 80° F.	17.5	0.3	17.5	0.3
P_4 (heat of combustion)		131.7		26.9
Additional heat required		-		62.77*
Total		136.0		136.0
Output:				
Exit gases at 1550° F.:				
N_2	47.4	36.9	4.0	3.1
H_2	-	-	0.85	9.1
O_2	6.3	4.9	-	-
H_2O	3.6	13.1	11.55	42.0
CaP_2O_6 at 1940° F.	30.5	36.1	30.5	36.1
Heat losses:				
vaporizer shell		12.3		12.3
grate cooling		10.4		10.4
radiation and convection		16.0		16.0
unaccounted for		6.3		7.0
Total		136.0		136.0

* This represents the additional heat requirement for the operation of the system using air plus steam for phosphorus oxidation.

The combustion of phosphorus in air is represented by the equation: P_4 (solid) + 5 O_2 (gas) = 2 P_2O_5 (solid) + 1,316,720 Btu., and the combustion of phosphorus in a mixture of air and steam is represented by the equation:

$$P_4 \text{ (solid)} + 0.74\ O_2 + 2.84\ N_2 + Ca_3(PO_4)_2 =$$
$$3\ CaP_2O_6 + 2.84\ N_2 + 8.52\ H_2 + 269{,}270 \text{ Btu.}$$

A comparison of the two heat balances shown in Table 9, indicates that there is an additional heat requirement of 62,770,000 Btu. for the process when using air plus steam oxidation. Supplying this additional heat appears to be the major difficulty to be overcome in the application of steam oxidation for phosphorus combustion in a metaphosphate furnace of present design. In the solution of this problem, some of the required heat might be added as superheat in the steam used for oxidation, but the balance of the heat would need to be furnished to the system by other means, possitbly by increasing the thermal insulation. Research is in progress to develop a suitable furnace and satisfactory conditions for carrying out the process.

A promising possible development in connection with the utilization of steam oxidation of phosphorus in the presence of a solid phosphate (phosphates other than rock phosphate might be used) would be the production of a product containing both ammonium and potassium metaphosphates. A product of this character might be designated as $K(NH_4)P_2O_6$, and would contain 22.9 percent potash (K_2O), 6.8 percent nitrogen (N_2), and 68.8 percent phosphoric acid (P_2O_5), or a total of 98.5 percent active fertilizer material, in the terms in which these are usually expressed. Obviously, also, the relative propotions of potash and nitrogen might be varied as desired between the limits of potassium metaphosphate and ammonium metaphosphate.

The synthesis of ammonia from the hydrogen and nitrogen probably would need be done outside of the furnace. Potassium metaphosphate containing an excess of phosphoric acid might be produced in the furnace and this product then might be neutralized with gaseous ammonia:

$KPO_3 + HPO_3 + NH_3 = K(NH_4)P_2O_6$.

That this would be practical is demonstrated by the fact that in present fertilizer-manufacturing operations ammonia is used to condition or neutralize the free acid content of phosphate fertilizer compounds, including both calcium and potassium metaphosphate.

On the basis of past experience, it appears probable that some very significant developments will be made utilizing steam oxidation of phosphorus in connection with the manufacture of metaphosphates and other phosphate materials.

An Evaluation of Phosphorus Combustion Processes

The developments in the science of utilizing phosphate materials, especially during the past ten years, have brought phosphorus to the status of an abundant industrial raw material. Prior to about 1933, it was produced only on a comparatively small scale and used by industry in limited quantities. The effects of its use in chemical warfare in the present war are tremendous, and it will have many new industrial uses when the war is over.

Inasmuch as phosphorus is used mostly in the form of its compounds, a large number of new processes and refinements of old processes have been developed for converting it into its compounds.

Phosphorus is produced either in the electric furnace or in the blast furnace in a vapor form accompanied by a large quantity of carbon monoxide. Although the entire gaseous furnace product may be burned to convert the phosphorus to its oxide, this treatment is basically uneconomic as the carbon monoxide is a valuable fuel. It is for this reason that the phosphorus is separated from the furnace exhaust gas and handled and burned separately. In addition to the conservation of the gas heating value, the isolation of solid phosphorus in phosphate processing has made available supplies of the material for use in warfare.

The comparatively new development of preferential oxidation of phosphorus will probably enjoy wide use in the era after the war. The process is at present in an advanced stage of pilot-plant development, and will be particularly applicable to blast-furnace practice where the phosphorus pentoxide produced by the oxidation may be converted to phosphoric acid and the carbon monoxide may be burned to preheat the blast in the furnace stoves.

Although steam oxidation of phosphorus is still in the research stage of development, there is a possibility that the method may be developed into a commercial process. The particular usefulness of this form of oxidation of phosphorus appears to lie in the manufacture of metaphosphates. The process would appear to be desirable to the fertilizer industry because the gaseous products may be used to synthesize ammonia. The ammonia thus produced could be used to make ammonium phosphates or various other ammoniated fertilizer compounds.

BIBLIOGRAPHY

A. Book:

1. Mellor, J. W. A comprehensive treatise of inorganic and theoretical chemistry. Second impression, v 8. Longmans-Green, 1940. pp. 771-782.

B. Periodicals:

1. Brunauer, S., and Shultz, J. F. Oxidation of phosphorus by steam. Ind. Eng. Chem. v. 33, pp. 828-832 (1941).
2. Copson, R. L., Newton, R. H., and Lindsay, J. W. Initial reaction between phosphate rock and phosphoric acid. Ind. Eng. Chem. v 29, pp. 175-179 (1937).
3. Copson, R. L., Pole, G. R., and Baskervill, W. H. Development of processes for metaphosphate productions. Ind. Eng. Chem. v 34, pp. 26-32 (1942).
4. Curtis, H. A. TVA makes H_3PO_4 electrically at Wilson Dam. Chem. Met. Eng. v 42, pp. 320-324 (1935).
5. Curtis, H. A. Making concentrated superphosphate at TVA fertilizer works. Chem. Met. Eng. v 42, pp. 488-491 (1935).
6. Curtis, H. A., Copson, R. L. and Abrams, A. J. Metaphosphate investigations aim at cheaper fertilizers. Chem. Met. Eng. v 44, pp. 140-142 (1937).
7. Curtis, H. A., Copson, R. L., Abrams, A. J., and Junkins, J. N. Full-scale production of metaphosphate achieved at Wilson Dam. Chem. Met. Eng. v 45, pp. 318-322 (1938).
8. Curtis, H. A., and Heaton, R. C. Design for a phosphate furnace. Chem. Met. Eng. v 45, pp. 536-540 (1938).
9. Curtis, H. A., and Miller, A. M. Operating observations at TVA fertilizer plant. Chem. Met. Eng. v 43, pp. 408-412 (1936).
10. Curtis, H. A., Miller, A. M., and Newton, R. H. TVA reviews its experience in phosphate smelting. Chem. Met. Eng. v 45, pp. 116-120 (1938).
11. Curtis, H. A., Miller, A. M., and Newton, R. H. Process developments at TVA phosphoric acid plant. Chem. Met. Eng. v 45, pp. 193-197 (1938).

12. Emmett, P. H., and Shultz, J. F. The oxidation of phosphorus to a pentavalent form by carbon dioxide. Ind. Eng. Chem. v 31, pp. 105-111 (1939).

13. Frear, G. L., Ogg, E. R., and Hull, L. H. Preferential oxidation of phosphorus in the presence of carbon monoxide. (In preparation).

14. Hardin, L. J., Oldham, F. D., and Hammond, J. W. Development of P_2O_5 insolubility in phosphate mixtures: The formation of fluorapatite and its cause. Ind. Eng. Chem. v 29, pp. 758-766 (1937).

15. Junkins, J. N., and Heaton, R. H. Instrumentation of a TVA electric furnace phosphoric acid plant. Instruments v 12, pp. 161-165 (1939).

16. Miller, A. M., and Junkins, J. N. TVA estimates favorable costs for concentrated superphosphate. Chem. Met. Eng. v 43, I. pp. 583-587 and II. pp. 647-650 (1936).

17. Newton, R. H. TVA's phosphate smelting results. Chem. Met. Eng. v 45, pp. 193-197 (1938).

18. Walthall, J. H., and Striplin, M. M. Superphosphoric acid by the absorption of phosphorus pentoxide vapor. Ind. Eng. Chem. v 33, pp. 995-1000 (1941).

C. Publications of Learned Societies:

1. Baskervill, W. H. The packed-tower collection of phosphoric acid. Trans. Am. Inst. Chem. Engrs. v 37, No. 1, pp. 79-94 (1941).

2. Curtis, H. A., Copson, R. L., Abrams, A. J., and Junkins, J. N. Manufacture of calcium metaphosphate in a full-scale unit. Trans. Am. Inst. Chem. Engrs. v 34, No. 3, pp. 287-313 (1938).

3. Ipatiev, V. N., and Usachev, P. V. The oxidation of phosphorus with water at high temperatures and pressures in the presence of alkalies. J. Am. Chem. Soc. v 57, pp. 300-302 (1935).

4. Melville, H. W. Inert gas effects in chain reactions. Trans. Faraday Soc. v 28, pp. 814-818 (1932).

D. U. S. Government Publications:

1. Curtis, H. A. General outline of activities. Chemical Engineering Report No. 1. Tennessee Valley Authority, Department of Chemical Engineering. 1940.

E. Foreign Publications:

1. Booy, I. J. Explosive gas reactions. Rec. trav. chim. v 49, pp. 866-875 (1930). C. A. v 24, p. 5159.

2. Bushmakin, I. N., Ruisakov, M. V., and Frost, A. V. The oxidation of red phosphorus with water at elevated temperatures and pressures. J. Applied Chem. (U.S.S.R.) v 6, pp. 577-587 (1933). C. A. v 28, p. 3678.

3. Bushmakin, I. N., Ruisakov, M. V., and Frost, A. V. The oxidation of yellow phosphorus at elevated temperatures and pressures. J. Applied Chem. (U.S.S.R.) v 6, pp. 588-606 (1933). C. A. v 28, p. 3678.

4. Fishbeck, K., and Eich, H. The ozone reaction in the oxidation of phosphorus. Ber. v 71B, pp. 520-532 (1938). C. A. v 32, p. 4414.

5. Ipatiev, V. N., and Freitag, G. The oxidation of phosphorus with water at elevated temperatures and pressures. Z. anorg. allgem. Chem. v 215, pp. 388-414 (1933). C. A. v 28, p. 1594.

6. King, D. W., and Ludlam, E. B. Chain theory of oxidation of phosphorus vapors. J. Chem. Soc. (British) Part II, pp. 1500-1503 (1938).

7. Semenov, N. The oxidation of phosphorus vapors at low temperatures. Z. Physik. v 46, pp. 109-131 (1927). C. A. v 22, p. 901.

8. Zagvozdkin, K. I., and Barilko, N. A. The rates of oxidation and the composition of products in phosphorus oxidation. J. Phys. Chem. (U.S.S.R.) v 14, pp. 505-512 (1940). C. A. v 35, p. 2058.

F. U. S. Patents:

1. Almond, L. H. The oxidation of crude phosphorus. 2,221,770 (1940).

2. Junkins, J. N. Oxidizing elemental phosphorus. 2,125,297 (1938).

3. Klugh, B. G. Electric furnace oxidation of phosphorus. 1,463,959 (1923).

4. Liljenroth, F. G. Oxidizing phosphorus. 1,594,372 (1926), and 1,673,691 (1928).

5. Miner, C. G. Oxy-compounds of phosphorus. 1,686,873 (1928).

6. Zinn, R. E. Oxidizing phosphorus. 1,991,916 (1935).

G. Foreign Patents:

1. Britzke, E. Power gas and phosphorus. Brit. patent 229,768 (1923).

2. Compagnie Nationale De Matieres Colorantes Et Manufactures De Produits Chimiques Du Nord Reunies, Etablissements Kuhlmann. Oxidation of phosphorus. French patent 635,432 (1927). C. A. v 24, p. 697.

3. Compagnie Nationale De Matieres Colorantes Et Manufactures De Produits Chimiques Du Nord Reunies, Etablissements Kuhlmann. Oxidation of phosphorus. French patent 635,501 (1927). C. A. v 22, p. 4738.

4. Kureodov, A. M., Ignatyuk, V. G. and Drennov, K. A. A continuously operated autoclave for the oxidation of phosphorus. Russian patent 27,381 (1931). C. A. v 27, p. 2258.

5. Liljenroth, F. G. Oxidizing phosphorus. Canadian patent 247,164 (1925).

INDEX

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